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(11) EP 0 802 243 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
22.10.1997 Bulletin 1997/43

(51) Int. Cl.<sup>6</sup>: C09D 5/16

(21) Application number: 97106277.3

(22) Date of filing: 16.04.1997

(84) Designated Contracting States:  
BE DE DK FI GB GR IT NL SE

(30) Priority: 17.04.1996 JP 95028/96

(71) Applicant: NOF CORPORATION  
Tokyo (JP)

(72) Inventors:  
• Itoh, Masayasu,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)  
• Fukuda, Shigeo,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)  
• Kawakami, Yoshihisa,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)

• Matsubara, Yoshiro,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)  
• Kawamura, Yasushi,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)  
• Masuoka, Shigeru,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)  
• Honda, Yoshihiro,  
c/o NOF CORPORATION  
Totsuka-ku, Yokohama-shi, Kanagawa (JP)

(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem.  
et al  
Hoffmann Eitle,  
Patent- und Rechtsanwälte,  
Arabellastrasse 4  
81925 München (DE)

### (54) Coating composition

(57) A coating composition comprising a rosin compound, a polymer containing organosilyl ester groups, and an antifoulant as essential components is disclosed. This rosin-based coating composition gives a coating film which forms no residue layer on the surface thereof over long-term immersion, is hence free from physical defects such as cracks and peeling and capable of maintaining a sufficiently high rate of film erosion and preventing the attachment of marine organisms over long, has satisfactory suitability for recoating, and has the satisfactory ability to prevent marine-organism attachment over the out-fitting period.

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## Description

FIELD OF THE INVENTION

5 The present invention relates to a coating composition for use in preventing the attachment of organisms to the surfaces of structures submerged in seawater.

BACKGROUND OF THE INVENTION

10 The surfaces of structures submerged in seawater such as ship bottoms, buoys, fishing nets (e.g., fixed nets and farming nets), underwater antifouling films, and various draft and drain pipes for cooling undergo various troubles as a result of the attachment of barnacles, mytilids, serpulids, algae, and the like. It is well known to coat submerged structure surfaces with paints capable of preventing the attachment of such marine organisms in order to prevent fouling by these organisms. The resins currently used in paints for the prevention of marine-organism attachment are roughly divided  
15 into hydrolyzable polymer type and rosin type.

The most typical hydrolyzable polymers are organotin polymers. The paints based on an organotin polymer function as follows. The coating film formed therefrom erodes as a result of the hydrolysis in seawater of organotin groups bonded to the polymer, whereby the coating film retains its surface activity. The organotin compound resulting from the hydrolysis also functions as an antifoulant. The coating film is thus capable of preventing the attachment of marine  
20 organisms over a long period of time. However, since organotin compounds tend to accumulate in the environment, use thereof is restricted from the standpoint of avoiding environmental pollution. Many proposals have been made on hydrolyzable polymers as substitutes for such organotin polymers in, e.g., JP-A-60-500452 (corresponding to WO 84/02915, PCT/US84/00068), JP-A-63-215780, and JP-A-7-102193 (corresponding to U.S. Patent 5,436,284). (The term "JP-A" as used herein means an "unexamined published Japanese patent application.")

25 On the other hand, the paints based on a rosin are advantageous in that since the rosin is slightly soluble in alkali solutions and dissolves into seawater, which is weakly alkaline ( $\text{pH} \approx 7.8\text{--}8.2$ ) (solubility in seawater with a  $\text{pH}$  of 8.1:  $8.6 \times 10^{-5}$  mol/l), an antifoulant can be effectively and gradually released into seawater. Due to their slight solubility in seawater, rosins are extensively used in antifouling paints for the prevention of marine-organism attachment. Methods of use thereof are described in many publications including, e.g., "Shikizai Kōgaku Handobukku (Colorant Engineering Handbook)" (pp. 821-, edited by the Colorant Society) and "Senpaku No Tosō To Toryō (Coating and Paints for Ships)"  
30 (pp. 70-, written by Manabu Nakao, the Ship Technology Society).

However, rosins themselves are physically brittle (have considerably poor film-forming ability due to their low molecular weights) and should be used as blends with other synthetic resins or the like in order to compensate for the brittleness. The blending ingredients used for compensating for the brittleness should be polymers having satisfactory  
35 compatibility with rosins. If a rosin is blended with a polymer poorly compatible therewith, the rosin and the polymer separate from each other and the resulting rosin phase exhibits its physical brittleness.

With respect to the blending of rosins with other polymers, proposals were made in JP-A-50-135125. Further, it was reported in JP-A-60-28456 that use of a blending polymer having satisfactory compatibility facilitates the control of coating film erodibility (self-polishing properties).

40 However, it was found that even when a blend of a rosin with a polymer satisfactorily compatible therewith is used in an antifouling paint, the coating film formed from the paint comes to have drawbacks after long-term immersion, such as a decrease in coating film erodibility, generation of physical defects in the coating film, and a decrease in the prevention of marine-organism attachment, although satisfactory in the initial properties thereof. Further, since ships, in particular, are recoated after a certain period (about from one to three years) of service, the old coating films are required  
45 to have suitability for recoating, i.e., the ability to be coated with a fresh paint. However, coating films formed from the prior art antifouling paints containing a blend of a rosin and a polymer compatible therewith were found to be unsuitable for this recoating.

These drawbacks and defect are attributable to the formation of a surface residue layer resulting from the dissolution (leaching) of the antifoulant together with the rosin on the coating film surface in preference to the rosin-compatible  
50 polymer due to the solubility in seawater of the polymer itself, which is lower than that of the rosin or is almost nil.

Blending polymers are required to have a higher film-forming ability than rosins, i.e., to have a higher molecular weight than rosins, because they are used in order to compensate for the physical brittleness of rosins. This difference in molecular weight between rosins and blending polymers results in a difference in solubility therebetween. Since the thickness of the residue layer increases with immersion time, this results in a decrease in coating film erodibility and  
55 generation of physical coating film defects due to internal cohesion within the residue layer. As a result of these, the effect of preventing marine-organism attachment is lessened and suitability for recoating is reduced.

As described above, despite the slight solubility of rosins in seawater which property is a performance rendering the rosins exceedingly suitable for use in paints for marine-organism attachment, there has so far been no coating composition which continuously takes advantage of that performance over a long period of time.

Furthermore, the hydrolyzable polymers proposed as substitutes for organotin polymers in JP-B-5-32433 (corresponding to JP-A-60-500452) and JP-A-63-215780, which have organosilicon groups as hydrolyzable groups, were found to have defects, for example, that the coating films comprising these polymers are unsuitable for the prevention of marine-organism attachment because they do not dissolve into seawater or they peel off during immersion in seawater. (The term "JP-B" as used herein means an "examined Japanese patent publication.") The present inventors made intensive studies in order to eliminate those defects and, as a result, found that the defects could be eliminated not by merely incorporating organosilyl groups but with the polymers described in JP-A-7-102193 (corresponding to U.S. Patent 5,436,284).

However, an investigation made thereafter revealed that even the polymers proposed in the reference cited just above are unsatisfactory not only in performances after long-term immersion in seawater, in particular suitability for recoating, but also in the prevention of marine-organism attachment over a period corresponding to the out-fitting period, which performance is required for out-fitting.

The term "out-fitting period" means the period in ship construction in which a hull constructed within a dock is floated on the seawater outside the dock and equipped for sailing. This period is usually about 3 months.

Since the hull is exposed in an anchored state to the sea near the dockyard (i.e., exposed to a sea area where severe fouling by organisms occurs unlike in the ocean) during the out-fitting period, the antifouling paint to be used for the out-fitting period is required to have a higher-than-ordinary degree of performance in the prevention of marine-organism attachment over the out-fitting period.

The ship which has been out-fitted is commissioned in service as it is or after being docked again and finished. If the attachment of organisms occurs during the out-fitting period, the ship having the adherent organisms cannot be commissioned in service because the ship has a reduced fuel efficiency from the initial stage of service. In the case of redocking the ship, it is necessary to remove the adherent organisms prior to service. If use of an antifouling paint has resulted in such troubles, the paint intended for the prevention of marine-organism attachment was utterly ineffective in performing its function, namely the application thereof was equal to nonuse thereof.

The present inventors devised a test method for evaluating the ability to prevent marine-organism attachment over the out-fitting period. Specifically, this improved test was conducted in the seawater of Owase bay, Mie, Japan, where fouling by marine organisms is severer than in Aioi Bay, Hyogo, Japan, a sea area usually used by the present inventors for evaluating the ability to prevent marine-organism attachment, for three months of from July to September, 1996 in such a manner that test pieces were immersed while being kept horizontal so as to be more influenced by sunlight, in contrast to the ordinary immersion in which test pieces are kept perpendicular to the water surface. Thus, the immersion test was initiated in summer, when fouling by organisms is severest (since an antifouling agent for preventing marine-organism attachment does not come to be leached immediately upon immersion but comes to be leached after a certain period, the possibility of organism attachment is high immediately after initiation of immersion when the test pieces are immersed in the season when fouling by organisms is severe). As a result of evaluation by this test method, the polymers described in JP-A-7-102193 (corresponding to U.S. Patent 5,436,284) were found to be unsatisfactory in the ability to prevent marine-organism attachment over the out-fitting period.

#### SUMMARY OF THE INVENTION

An object of the present invention is to develop a rosin-based coating composition giving a coating film which forms no residue layer on the surface thereof over long-term immersion, is hence free from physical defects such as cracks and peeling and capable of maintaining a sufficiently high rate of coating film erosion and preventing the attachment of marine organisms over a long period of time, and has satisfactory suitability for recoating and the satisfactory ability to prevent marine-organism attachment over the out-fitting period.

The present inventors directed attention to the following points in order to develop the desired coating composition. For developing the desired coating composition, it is necessary to enable the formation of a coating film which forms no residue layer on the surface thereof. In order for a coating film to satisfy this requirement, the coating film should contain a rosin-compatible polymer which comes to have enhanced solubility in seawater after immersion therein. Only polymers which undergo a chemical change upon immersion in seawater can perform such a function. Namely, such polymers undergoing a chemical change can have good compatibility with rosin resins before immersion in seawater and become hydrophilic only at the coating film surface after immersion in seawater to thereby retain a satisfactory dissolution rate.

The present inventors directed attention to, as a blending polymer, a polymer containing a carboxylic acid protected by an organosilyl group. This polymer is compatible with rosins (lowly polar) due to the low polarity of the organosilyl group and, after immersion in seawater, undergoes a chemical change due to the hydrolyzability of the organosilyl group. Thus, the seawater dissolution characteristics of the polymer dramatically change from insoluble to soluble. Organotin polymers having similar hydrolyzability are poorly compatible with rosins because of their higher polarity than the silylated polymer and are hence unable to perform the function of the silylated polymer. The crucially important properties required of a polymer for use as blends with rosins are low polarity and hydrolyzability in seawater.

As a result of intensive studies made by the present inventors on the above points, it has been found that the problems of prior art techniques can be completely eliminated by using a rosin compound such as a rosin or a derivative thereof in combination with a polymer containing organosilyl ester groups in which the organosilyl groups function as hydrolysis sites and with an antifoulant. Namely, they have succeeded in developing a rosin-based coating composition giving a coating film which forms no residue layer on the surface thereof over long-term immersion, is hence free from physical defects such as cracks and peeling and capable of maintaining a sufficiently high rate of coating film erosion and preventing the attachment of marine organisms over long, and has satisfactory suitability for recoating and the satisfactory ability to prevent marine-organism attachment over the out-fitting period.

The present invention provides a coating composition comprising, as essential components, (A) at least one rosin compound selected from rosins, rosin derivatives, and rosin metal salts, (B) at least one polymer containing organosilyl ester groups which comprises a polymer of at least one of monomers M represented by the formula



wherein  $R^1$  to  $R^3$  may be the same or different and each represents an alkyl group or an aryl group, and X represents an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group, a fumaroyloxy group, an itaconoyloxy group, or a citraconoyloxy group and/or a polymer of at least one of said monomers M and at least of polymerizable monomers other than said monomers M, and (C) an antifoulant.

#### DETAILED DESCRIPTION OF THE INVENTION

The rosin compound of ingredient A used as an essential component in the present invention is at least one selected from rosins, rosin derivatives, and rosin metal salts. Examples of the rosins include tall rosin, gum rosin, and wood rosin. Examples of the rosin derivatives include hydrogenated rosins, modified rosins obtained by reacting rosins with maleic anhydride, formylated rosins, and polymerized rosins. Examples of the rosin metal salts include zinc rosinate, calcium rosinate, copper rosinate, magnesium rosinate, and products of the reaction of rosins with compounds of other metals.

At least one selected from such rosin compounds is used in the present invention in such an amount that the proportion of this rosin compound to the polymer containing organosilyl ester groups of ingredient B is usually from 1/99 to 99/1, preferably from 5/95 to 95/5, by weight on a solid basis. If the amount of ingredient A is too small (i.e., the ratio of ingredient A to ingredient B is less than 1:99), the effect of preventing the attachment of marine organisms, in particular the effect of preventing marine-organism attachment over the out-fitting period, is not expected. If the amount thereof is too large (i.e., the ratio of ingredient A to ingredient B is larger than 99:1), the coating composition has reduced film-forming ability and gives a coating film which is apt to develop defects such as cracks and peeling and hence be less effective in the prevention of marine-organism attachment.

The polymer containing organosilyl ester groups of ingredient B used as another essential component in the coating composition of the present invention comprises a polymer of at least one of monomers M, which are represented by formula (1) described above, and/or a polymer of at least one of monomers M and at least one of polymerizable monomers other than monomers M.

As apparent from formula (1), monomers M each has a molecular structure comprising an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group [mostly a maleinoyloxy group monoesterified with an alkyl (having 1 to 6 carbon atoms)], a fumaroyloxy group [mostly a fumaroyloxy group monoesterified with an alkyl (having 1 to 6 carbon atoms)], an itaconoyloxy group [mostly an itaconoyloxy group monoesterified with an alkyl (having 1 to 6 carbon atoms)], or a citraconoyloxy group [mostly a citraconoyloxy group monoesterified with an alkyl (having 1 to 6 carbon atoms)] as an unsaturated group (X) and a triorganosilyl group.

In the triorganosilyl group, the three alkyl or aryl groups ( $R^1$  to  $R^3$ ) may be the same or different. Examples thereof include linear or branched alkyl groups having up to 20 carbon atoms, such as methyl, ethyl, propyl, and butyl;

cycloalkyl groups such as cyclohexyl and substituted cyclohexyls; and aryl groups and substituted aryl groups. Examples of the substituted aryl groups include aryl groups substituted with at least one substituent selected from halogens, alkyl groups having 1 to about 8 carbon atoms, acyl groups, a nitro group, an amino group, and the like.

Of such monomers M, those having a (meth)acryloyloxy group in the molecule include trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, and tribenzylsilyl (meth)acrylate.

Other examples of the monomers M having a (meth)acryloyloxy group in the molecule include ethyldimethylsilyl (meth)acrylate, n-butyltrimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, diisopropylstearyltrimethylsilyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butylidiphenylsilyl (meth)acrylate, lauryldiphenylsilyl (meth)acrylate, and t-butyl-m-nitrophenylmethylsilyl (meth)acrylate.

Examples of the monomers M having a maleinoyloxy group in the molecule include trimethylsilyl methyl maleate, triethylsilyl ethyl maleate, tri-n-propylsilyl n-propyl maleate, tri-n-butylsilyl n-butyl maleate, tri-n-amylsilyl n-amyl maleate, tri-n-hexylsilyl n-hexyl maleate, tri-n-octylsilyl dodecyl maleate, tri-n-dodecylsilyl methyl maleate, triphenylsilyl methyl maleate, tri-p-tolylsilyl ethyl maleate, triisopropylsilyl isoamyl maleate, triisobutylsilyl phenyl maleate, t-butylidimethylsilyl methyl maleate, t-butylidiphenylsilyl methyl maleate, and n-octyldi-n-butylsilyl methyl maleate.

Examples of the monomers M having a fumaroyloxy group in the molecule include trimethylsilyl methyl fumarate, triethylsilyl ethyl fumarate, tri-n-propylsilyl n-propyl fumarate, tri-n-butylsilyl n-butyl fumarate, tri-n-amylsilyl n-amyl fumarate, tri-n-hexylsilyl n-hexyl fumarate, tri-n-octylsilyl dodecyl fumarate, tri-n-dodecylsilyl methyl fumarate, triphenylsilyl methyl fumarate, tri-p-methylphenylsilyl methyl fumarate, triisopropylsilyl methyl fumarate, triisobutylsilyl methyl fumarate, tri-2-chloroisopropylsilyl methyl fumarate, tri-t-butylsilyl methyl fumarate, ethyldimethylsilyl methyl fumarate, n-butyltrimethylsilyl methyl fumarate, and n-octyldi-n-butylsilyl methyl fumarate.

Examples of the monomers M having an itaconoyloxy group in the molecule include trimethylsilyl methyl itaconate, triethylsilyl ethyl itaconate, tri-n-propylsilyl n-propyl itaconate, tri-n-butylsilyl n-butyl itaconate, tri-n-amylsilyl n-amyl itaconate, tri-n-hexylsilyl n-hexyl itaconate, tri-n-octylsilyl dodecyl itaconate, tri-n-dodecylsilyl methyl itaconate, triphenylsilyl methyl itaconate, tri-p-fluorophenylsilyl methyl itaconate, triisopropylsilyl methyl itaconate, triisobutylsilyl methyl itaconate, tri-2-cyanoisopropylsilyl methyl itaconate, tri-t-butylsilyl methyl itaconate, ethyldimethylsilyl methyl itaconate, n-butyltrimethylsilyl methyl itaconate, and n-octyldi-n-butylsilyl methyl itaconate.

Examples of the monomers M having a citraconoyloxy group in the molecule include trimethylsilyl methyl citraconate, triethylsilyl ethyl citraconate, tri-n-propylsilyl n-propyl citraconate, tri-n-butylsilyl n-butyl citraconate, tri-n-amylsilyl n-amyl citraconate, tri-n-hexylsilyl n-hexyl citraconate, tri-n-octylsilyl dodecyl citraconate, tri-n-dodecylsilyl methyl citraconate, triphenylsilyl methyl citraconate, tri-p-hydroxyphenylsilyl methyl citraconate, triisopropylsilyl methyl citraconate, triisobutylsilyl methyl citraconate, tri-2-bromoisopropylsilyl methyl citraconate, tri-t-butylsilyl methyl citraconate, ethyldimethylsilyl methyl citraconate, n-butyltrimethylsilyl methyl citraconate, and n-octyldi-n-butylsilyl methyl citraconate.

The polymerizable monomers other than monomers M are monomers copolymerizable with monomers M. Examples thereof include acrylic acid and acrylic esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate, t-butyl acrylate, s-butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, glycidyl acrylate, 2-methoxyethyl acrylate, and 2-ethoxyethyl acrylate; and methacrylic acid and methacrylic esters such as methyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, s-butyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, glycidyl methacrylate, 2-methoxyethyl methacrylate, and 2-ethoxyethyl methacrylate.

Other examples of the polymerizable monomers include vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, and VeoVa 9 and VeoVa 10 (trade names; manufactured by Showa Shell Kagaku K.K., Japan), maleic esters such as dimethyl maleate, diethyl maleate, di-n-propyl maleate, diisopropyl maleate, and di-2-methoxyethyl maleate, fumaric esters such as dimethyl fumarate, diethyl fumarate, di-n-propyl fumarate, diisopropyl fumarate, and di-2-methoxyethyl fumarate, crotonic esters, itaconic esters, citraconic esters, styrene, vinyltoluene,  $\alpha$ -methylstyrene, and acrylonitrile.

In producing the polymer containing organosilyl ester groups of ingredient B, the proportion of at least one of monomers M represented by formula (1) to at least one polymerizable monomer other than monomers M can be suitably determined according to the use of the coating composition. In general, however, the proportion of at least one of monomers M is preferably from 1 to 100% by weight and that of at least one other monomer is preferably from 99 to 0% by weight.

The polymer containing organosilyl ester groups of ingredient B can be obtained by polymerizing such a monomer mixture in the presence of a polymerization catalyst by any of various methods such as solution polymerization, bulk polymerization, emulsion polymerization, and suspension polymerization in an ordinary way. In preparing a coating composition using this polymer containing organosilyl ester groups of ingredient B, the polymer is preferably diluted with an organic solvent to give a polymer solution having an appropriate viscosity. From this standpoint, it is desirable to employ solution polymerization or bulk polymerization.

Examples of the polymerization catalyst include azo compounds such as azobisisobutyronitrile and triphenylmethy-lazobenzene and peroxides such as benzoyl peroxide, di-t-butyl peroxide, t-butyl peroxybenzoate, and t-butyl peroxyisopropylcarbonate.

Examples of the organic solvent include aromatic hydrocarbons such as xylene and toluene, aliphatic hydrocarbons such as hexane and heptane, esters such as ethyl acetate and butyl acetate, alcohols such as isopropyl alcohol and butyl alcohol, ethers such as dioxane and diethyl ether, and ketones such as methyl ethyl ketone and methyl isobutyl ketone. These compounds are used alone or as a mixture of two or more thereof.

The thus-obtained polymer containing organosilyl ester groups of ingredient B desirably has a weight-average molecular weight of from 1,000 to 150,000. If the molecular weight thereof is too low (i.e., less than 1,000), it is difficult to form a normal film. If the molecular weight thereof is too high (i.e., more than 150,000), the coating composition obtained using the polymer has too high a viscosity and should hence be diluted with a thinner. Such a diluted coating composition is disadvantageous in that since the coating film thickness obtainable per coating operation is small, a larger number of coating operations are necessary. The solution of the polymer of ingredient B desirably has a viscosity of 150 P or lower at 25°C. For attaining such a viscosity, the polymer solution of ingredient B is desirably regulated so as to have a solid content of from 5 to 90% by weight, preferably from 15 to 85% by weight.

Ingredient (C) used as the last essential component in the coating composition of the present invention is an anti-foulant. This ingredient can be selected from a wide variety of conventionally known antifoulant compounds, which are roughly divided into three groups, i.e., inorganic compounds, organometallic compounds, and metal-free organic compounds. Examples of the inorganic compounds include copper powder, copper compounds such as cuprous oxide, cuprous thiocyanate, copper carbonate, copper chloride, and copper sulfate, zinc sulfate, zinc oxide, nickel sulfate, and copper-nickel alloys.

The organometallic compounds include, for example, organocopper compounds, organonickel compounds, and organozinc compounds. Also usable are maneb, manzeb, propineb, and the like. Examples of the organocopper compounds include oxine copper, copper nonylphenolsulfonate, copper bis(ethylenediamine) bis(dodecylbenzenesulfonate), copper acetate, copper naphthenates, copper bis(pentachlorophenolate)s, and copper pyrrhione. Examples of the organonickel compounds include nickel acetate and nickel dimethyldithiocarbamate. Examples of the organozinc compounds include zinc acetate, zinc carbamate, zinc dimethyldithiocarbamate, zinc pyrrhione, and zinc ethylenebis-dithiocarbamate.

The metal-free organic compounds include, for example, N-trihalomethylthiophthalimides, dithiocarbamic acids, N-arylmaleimides, 3-(substituted amino)-1,3-thiazolidine-2,4-diones, dithiocyano compounds, triazine compounds, and others.

Examples of the N-trihalomethylthiophthalimides include N-trichloromethylthiophthalimide and N-fluorodichloromethylthiophthalimide. Examples of the dithiocarbamic acids include bis(dimethylthiocarbamoyl) disulfide, ammonium N-methyldithiocarbamate, ammonium ethylenebis(dithiocarbamate), and milneb.

Examples of the N-arylmaleimides include N-(2,4,6-trichlorophenyl)maleimide, N-4-tolylmaleimide, N-3-chlorophenylmaleimide, N-(4-n-butylphenyl)maleimide, N-(anilinophenyl)maleimide, and N-(2,3-xylyl)maleimide.

Examples of the 3-(substituted amino)-1,3-thiazolidine-2,4-diones include 3-benzylideneamino-1,3-thiazolidine-2,4-dione, 3-(4-methylbenzylideneamino)-1,3-thiazolidine-2,4-dione, 3-(2-hydroxybenzylideneamino)-1,3-thiazolidine-2,4-dione, 3-(4-dimethylaminobenzylideneamino)-1,3-thiazolidine-2,4-dione, and 3-(2,4-dichlorobenzylideneamino)-1,3-thiazolidine-2,4-dione.

Examples of the dithiocyano compounds include dithiocyanomethane, dithiocyanoethane, and 2,5-dithiocyanothiophene. Examples of the triazine compounds include 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine.

Examples of the other metal-free organic compounds include 2,4,5,6-tetrachloroisophthalonitrile, N,N-dimethyl-N'-dichlorophenylurea, 4,5-dichloro-2-n-octylisothiazolin-3-one, N,N-dimethyl-N'-phenyl(N-fluorodichloromethylthio)sulfamide, tetramethylthiuram disulfide, 3-iodo-2-propynylbutyl carbamate, 2-(methoxycarbonylamino)benzimidazole, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, diiodomethyl p-tolyl sulfone, phenyl(bispyridine)bismuth dichloride, 2-(4-thiazolyl)benzimidazole, and pyridine triphenylborane.

At least one member selected from such various antifoulants is used in the present invention in an amount of usually from 0.1 to 80% by weight, preferably from 1 to 60% by weight, based on the total amount of all solid ingredients in the coating composition. If the amount of the antifoulant is too small (i.e., less than 0.1% by weight), an antifouling effect cannot be expected. If the amount thereof is too large (i.e., more than 80% by weight), the coating film formed from the coating composition is apt to develop defects such as cracks and peeling and be less effective in fouling prevention.

Various additive ingredients may be suitably incorporated into the coating composition of the present invention thus prepared. Examples of the optional ingredients include colorants such as pigments, e.g., red iron oxide, zinc oxide, and talc, and dyes, dehumidifiers, and additives ordinarily employed in paints, such as antisludging agents, plasticizers, e.g., chlorinated paraffins, dioctyl phthalate, and tricresyl phosphate, ultraviolet absorbers, e.g., benzophenone compounds and benzotriazole compounds, antiflooding agents, antisetling agents, antifoaming agents, silanols, polysiloxanes, and alkoxysilanes.

For forming an antifouling coating film from the coating composition of the present invention on the surface of a

structure to be submerged in seawater, use may be made of a method in which the coating composition is applied on the surface in a suitable manner and the solvent is removed by evaporation at ordinary temperature or with heating. By this method, a dry coating film can be easily formed on the surface of the structure.

- 5 The present invention will be explained below in more detail by reference to Preparation Examples, Examples, and Comparative Examples. In these examples, all parts are by weight, and the molecular weights are given in terms of weight-average molecular weight measured by GPC (gel permeation chromatography) and calculated for standard polystyrene. Further, monomers  $M_1$  to  $M_9$ , used in Preparation Examples, are monomers  $M$  represented by formula (1) wherein  $R^1$  to  $R^3$  and  $X$  are as shown in Table 1.

Table 1

	Organic Groups in Formula (1)			
	$R^1$	$R^2$	$R^3$	$X$
15 Monomer $M_1$	$CH_3$	$CH_3$	$t-C_4H_9$	$CH_2=CHCOO$
Monomer $M_2$	$i-C_3H_7$	$i-C_3H_7$	$i-C_3H_7$	$CH_2=CHCOO$
Monomer $M_3$	$n-C_4H_9$	$n-C_4H_9$	$n-C_4H_9$	$CH_2=C(CH_3)COO$
20 Monomer $M_4$	$C_6H_5$	$C_6H_5$	$t-C_4H_9$	$CH_2=C(CH_3)COO$
Monomer $M_5$	$i-C_3H_7$	$i-C_3H_7$	$i-C_3H_7$	$CH_2=C(CH_3)COO$
Monomer $M_6$	$i-C_3H_7$	$i-C_3H_7$	$i-C_3H_7$	$i-C_5H_{11}OOCCH=CHCOO$ (maleinoyloxy group)
Monomer $M_7$	$C_6H_5$	$C_6H_5$	$t-C_4H_9$	$CH_3OOCCH=CHCOO$ (fumaroyloxy group)
25 Monomer $M_8$	$n-C_4H_9$	$n-C_4H_9$	$n-C_4H_9$	$CH_2=C(CH_2COO-n-C_5H_{11})COO$ (itaconoyloxy group)
Monomer $M_9$	$n-C_{20}H_{41}$	$p-CH_3-C_6H_4$	$m-Cl-C_6H_4$	$n-C_6H_{13}OOCCH(CH_3)=CHCOO$ (citraconoyloxy group)

#### PREPARATION EXAMPLES 1 TO 4

- 35 According to the formulations shown in Table 2, a solvent  $a$  was introduced into a flask equipped with a stirrer and then heated to a given reaction temperature, and a mixture of a monomer  $M$ , one or more other monomers, and a polymerization catalyst  $a$  was added dropwise to the solvent in the flask with stirring over a period of 3 hours. After completion of the addition, the reaction mixture was kept at that temperature for 30 minutes. Subsequently, a mixture of a solvent  $b$  and a polymerization catalyst  $b$  was added dropwise thereto over a period of 20 minutes, and the resulting mixture was continuously stirred at that temperature for 2 hours to complete the polymerization reaction. A diluting solvent was finally added for dilution. Thus, polymer solutions  $S_1$  to  $S_4$  were obtained.

#### PREPARATION EXAMPLES 5 TO 8

- 45 Into a heat- and pressure-resistant vessel were introduced a monomer  $M$ , other monomers, and a polymerization catalyst according to the formulations shown in Table 3. The vessel was completely closed, and the contents were heated to a given reaction temperature with shaking and were then continuously shaken at that temperature for 8 hours to complete the reaction. Subsequently, a diluting solvent was added and the resulting mixture was shaken for 1 hour to dissolve the reaction product. Thus, polymer solutions  $S_5$  to  $S_8$  were obtained.

#### PREPARATION EXAMPLES 9 TO 16

- 50 Into a flask equipped with a stirrer were introduced a solvent, one or more monomers  $M$ , other monomers, and a polymerization catalyst according to the formulations shown in Tables 4 and 5. The contents were heated to a given temperature with stirring and then continuously stirred at that temperature for 6 hours to complete the reaction. Subsequently, the reaction mixture was diluted with a diluting solvent. Thus, polymer solutions  $S_9$  to  $S_{16}$  were obtained.

In Tables 2 to 5, "Veova 9" and "Veova 10" (trade names of Showa Shell Kagaku K.K.) each is a vinyl ester monomer, and "Perbutyl I" (registered trademark in Japan of NOF CORPORATION) is an organic peroxide.

Table 2

			Preparation Example			
			1	2	3	4
Formulation (parts)	Solvent a	xylene butyl acetate	40 -	40 10	- 40	30 -
	Monomers M	monomer M <sub>1</sub>	50	-	-	-
		monomer M <sub>2</sub>	-	30	-	-
		monomer M <sub>3</sub>	-	-	50	-
		monomer M <sub>4</sub>	-	-	-	10
		monomer M <sub>5</sub>	-	-	-	-
		monomer M <sub>6</sub>	-	-	-	-
		monomer M <sub>7</sub>	-	-	-	-
		monomer M <sub>8</sub>	-	-	-	-
		monomer M <sub>9</sub>	-	-	-	-
	Other monomers	methyl methacrylate	-	70	40	-
		n-butyl methacrylate	30	-	-	-
		2-methoxyethyl methacrylate	-	-	-	5
		n-butyl acrylate	-	-	-	5
2-ethylhexyl acrylate		10	-	-	-	
2-methoxyethyl acrylate		-	-	-	-	
acrylic acid		-	-	-	-	
vinyl acetate		-	-	-	30	
vinyl propionate		-	-	-	-	
vinyl benzoate		-	-	-	-	
Veova 9		-	-	-	10	
Veova 10		-	-	-	-	
dimethyl maleate		-	-	-	10	
di-2-methoxyethyl maleate		-	-	-	-	
styrene		-	-	-	30	
$\alpha$ -methylstyrene	10	-	10	-		
Polymerization catalyst a	azobisisobutyronitrile	-	-	-	5	
	Perbutyl I	1	1	1	-	
Solvent b	xylene	10	10	10	10	
Polymerization catalyst b	azobisisobutyronitrile	-	-	-	1	
	Perbutyl I	1	1	1	-	
Diluting solvent	xylene	47	38	16	30	
	butyl acetate	-	-	31	-	
Reaction temperature (°C)			140	135	126	80
Solid concentration (wt%)			50	50	50	50
Molecular weight of polymer (x 1,000)			35	42	96	40
Symbol of polymer solution			S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>



Table 3

5				Preparation Example			
				5	6	7	8
	Formulation (parts)	Monomers M	monomer M <sub>1</sub>	-	-	-	-
			monomer M <sub>2</sub>	-	-	-	60
10			monomer M <sub>3</sub>	-	-	-	-
			monomer M <sub>4</sub>	-	-	-	-
			monomer M <sub>5</sub>	80	-	-	-
			monomer M <sub>6</sub>	-	50	-	-
15			monomer M <sub>7</sub>	-	-	20	-
			monomer M <sub>8</sub>	-	-	-	5
			monomer M <sub>9</sub>	-	-	-	-
20		Other monomers	methyl methacrylate	15	-	10	25
			n-butyl methacrylate	-	-	-	-
			2-methoxyethyl methacrylate	-	-	-	-
25			n-butyl acrylate	-	-	-	-
			2-ethylhexyl acrylate	5	-	-	-
			2-methoxyethyl acrylate	-	-	50	10
			acrylic acid	-	-	-	-
30			vinyl acetate	-	10	-	-
			vinyl propionate	-	5	-	-
			vinyl benzoate	-	-	20	-
35			Veova 9	-	-	-	-
			Veova 10	-	5	-	-
			dimethyl maleate	-	20	-	-
40			di-2-methoxyethyl maleate	-	-	-	-
			styrene	-	-	-	-
			$\alpha$ -methylstyrene	-	10	-	-
		Polymerization catalyst	azobisisobutyronitrile	-	-	2	2
45			Perbutyl I	2	2	-	-
		Diluting solvent	xylene	98	70	98	63
			butyl acetate	-	28	-	35
	Reaction temperature (°C)			120	120	80	80
50	Solid concentration (wt%)			50	50	50	50
	Molecular weight of polymer (x 1,000)			32	15	8	6
	Symbol of polymer solution			S <sub>5</sub>	S <sub>6</sub>	S <sub>7</sub>	S <sub>8</sub>

55

Table 4

			Preparation Example				
			9	10	11	12	
5	Formulation (parts)	Solvent	xylene	44	50	25	40
			butyl acetate	-	-	10	-
10	Monomers M	monomer M <sub>1</sub>	-	1	-	-	
		monomer M <sub>2</sub>	-	-	100	-	
		monomer M <sub>3</sub>	-	-	-	20	
		monomer M <sub>4</sub>	-	-	-	-	
15		monomer M <sub>5</sub>	-	-	-	-	
		monomer M <sub>6</sub>	-	-	-	-	
		monomer M <sub>7</sub>	-	-	-	-	
		monomer M <sub>8</sub>	50	-	-	30	
20		monomer M <sub>9</sub>	5	-	-	-	
		Other monomers	methyl methacrylate	-	-	-	-
25		n-butyl methacrylate	-	30	-	-	
		2-methoxyethyl methacrylate	-	-	-	-	
		n-butyl acrylate	20	-	-	-	
		2-ethylhexyl acrylate	-	-	-	-	
30		2-methoxyethyl acrylate	-	-	-	-	
		acrylic acid	-	-	-	-	
		vinyl acetate	-	40	-	-	
		vinyl propionate	-	-	-	-	
35		vinyl benzoate	-	-	-	30	
		Veova 9	10	-	-	-	
		Veova 10	15	-	-	-	
		dimethyl maleate	-	-	-	-	
40		di-2-methoxyethyl maleate	-	-	-	20	
		styrene	-	10	-	-	
45		α-methylstyrene	-	19	-	-	
		Polymerization catalyst	azobisisobutyronitrile	-	-	-	-
		Perbutyl I	1	2	1	2	
		Diluting solvent	xylene	55	36	64	48
50		butyl acetate	-	12	-	10	
		Reaction temperature (°C)		120	110	135	140
		Solid concentration (wt%)		50	50	50	50
		Molecular weight of polymer (x 1,000)		125	11	21	40
55	Symbol of polymer solution		S <sub>9</sub>	S <sub>10</sub>	S <sub>11</sub>	S <sub>12</sub>	

Table 5

5				Preparation Example			
				13	14	15	16
	Formulation (parts)	Solvent	xylene	44	30	35	40
			butyl acetate	-	10	-	-
10		Monomers M	monomer M <sub>1</sub>	-	-	5	-
			monomer M <sub>2</sub>	5	-	10	-
			monomer M <sub>3</sub>	-	-	-	10
			monomer M <sub>4</sub>	-	25	10	-
15			monomer M <sub>5</sub>	5	-	-	-
			monomer M <sub>6</sub>	-	-	-	50
			monomer M <sub>7</sub>	-	25	-	-
20			monomer M <sub>8</sub>	-	-	-	10
			monomer M <sub>9</sub>	-	-	-	5
		Other monomers	methyl methacrylate	50	-	25	-
25			n-butyl methacrylate	5	-	-	-
			2-methoxyethyl methacrylate	5	-	19	-
			n-butyl acrylate	-	20	30	-
			2-ethylhexyl acrylate	10	-	-	-
30			2-methoxyethyl acrylate	20	-	-	5
			acrylic acid	-	-	1	-
			vinyl acetate	-	-	-	-
35			vinyl propionate	-	30	-	-
			vinyl benzoate	-	-	-	-
			Veova 9	-	-	-	10
40			Veova 10	-	-	-	-
			dimethyl maleate	-	-	-	-
			di-2-methoxyethyl maleate	-	-	-	-
			styrene	-	-	-	10
45			$\alpha$ -methylstyrene	-	-	-	-
		Polymerization catalyst	azobisisobutyronitrile	-	-	0.5	2
			Perbutyl I	5	5	-	-
50		Diluting solvent	xylene	51	55	52	58
			butyl acetate	-	-	12.5	-
	Reaction temperature (°C)			120	143	70	80
	Solid concentration (wt%)			50	50	50	50
	Molecular weight of polymer (x 1,000)			5	1	147	102
55	Symbol of polymer solution			S <sub>13</sub>	S <sub>14</sub>	S <sub>15</sub>	S <sub>16</sub>

EXAMPLES 1 TO 20

Polymer solutions S<sub>1</sub> to S<sub>16</sub> each was mixed with various ingredients according to the formulations shown in Tables 6 to 10 (the numerals indicating ingredient amounts are given in terms of wt%). The resulting mixtures each was homogenized with a homomixer at 2,000 rpm. Thus, twenty coating compositions were prepared.

COMPARATIVE EXAMPLES 1 TO 6

"Laroflex MP-15" (trade name of BASF AG; vinyl chloride resin), "Pliolite S-5B" (trade name of The Goodyear Tire & Rubber Company; styrene-butadiene rubber), "Toyoparax A-70" (trade name of Tosoh Corp., Japan; chlorinated paraffin resin), and "Polysol EVA-AD-3" (trade name of Showa Highpolymer Co., Ltd., Japan; ethylene/vinyl acetate copolymer) each was mixed with various ingredients according to the formulations shown in Table 11 (the numerals indicating ingredient amounts are given in terms of wt%). The resulting mixtures each was homogenized with a homomixer at 2,000 rpm. Thus, three coating compositions were prepared.

In Tables 6 to 11, "Dimerex" (trade name of Hercules Inc.) is a polymerized rosin, "Disparlon A630-20X" and "Disparlon 4300" (trade names of Kusumoto Chemicals Ltd., Japan) and "Bentone SD-2" (trade name of Rheox, Inc.) each is an antisagging agent, "KMP590" (trade name of Shin-Etsu Chemical Co., Ltd., Japan) is a silicone resin powder, and "Tinuvin 900" (trade name of Ciba-Geigy Ltd.) is an ultraviolet absorber.

Table 6

		Example			
		1	2	3	4
Ingredient A	tall rosin	10	-	-	-
	gum rosin	-	-	10	30
	wood rosin	-	5	-	-
	Dimerex	-	-	-	-
	hydrogenated rosin	-	-	-	-
Ingredient B	polymer solution S <sub>1</sub>	20	10	-	-
	polymer solution S <sub>2</sub>	-	-	45	20
	polymer solution S <sub>3</sub>	-	20	-	-
	polymer solution S <sub>4</sub>	-	-	-	-
	polymer solution S <sub>5</sub>	-	-	-	20
	polymer solution S <sub>6</sub>	-	-	-	-
	polymer solution S <sub>7</sub>	-	-	-	-
	polymer solution S <sub>8</sub>	-	-	-	-
	polymer solution S <sub>9</sub>	-	-	-	-
Ingredient C	cuprous oxide	5	-	36	5
	copper thiocyanate	-	20	-	-
	Cu-Ni solid solution alloy	-	-	-	5
	N,N-dimethylchlorophenylurea	-	10	-	-
	4,5-dichloro-2-n-octylisothiazolin-3-one	10	-	-	-
	2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine	-	10	-	-
	2-pyridinethiol-1-oxide zinc salt	-	-	2	-
	2,4,6-trichlorophenylmaleimide	3	-	-	-
	3-iodo-2-propynylbutyl carbamate	5	-	-	-
Plasticizer	chlorinated paraffin	-	-	-	-
	tricresyl phosphate	-	-	-	-
Pigment	talc	-	-	-	2
	red iron oxide	3	5	2	1
	zinc oxide	-	3	-	1
	titanium dioxide	-	1	1	1
Antisagging agent	Disparlon A630-20X	2	2	2	3
	Bentone SD-2	1	-	1	-
Additive	trimethyl silanol	-	-	-	-
	KMP590	-	-	-	-
	Tinuvin 900	-	-	-	-
Solvent	xylene	31	14	2	12
	butyl acetate	10	-	-	-
Total		100	100	100	100

Table 7

		Example			
		5	6	7	8
Ingredient A	tall rosin	-	-	-	-
	gum rosin	-	5	-	12
	wood rosin	-	10	-	-
	Dimerex	20	-	-	-
	hydrogenated rosin	-	-	55	-
Ingredient B	polymer solution S <sub>1</sub>	-	-	-	-
	polymer solution S <sub>2</sub>	-	-	-	-
	polymer solution S <sub>3</sub>	-	-	-	-
	polymer solution S <sub>4</sub>	40	-	-	-
	polymer solution S <sub>5</sub>	-	30	5	-
	polymer solution S <sub>6</sub>	-	-	-	25
	polymer solution S <sub>7</sub>	-	-	-	-
	polymer solution S <sub>8</sub>	-	-	10	-
	polymer solution S <sub>9</sub>	-	-	-	-
Ingredient C	cuprous oxide	-	30	-	20
	copper thiocyanate	10	10	-	-
	Cu-Ni solid solution alloy	-	-	-	-
	2,4,5,6-tetrachloroisophthalonitrile	10	-	-	-
	N-(fluorodichloromethylthio)phthalimide	-	-	-	20
	2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine	10	-	-	-
	2-pyridinethiol-1-oxide zinc salt	-	-	2	-
	2-pyridinethiol-1-oxide copper salt	-	2	-	-
	3-iodo-2-propynylbutyl carbamate	-	-	2	-
Plasticizer	chlorinated paraffin	3	-	-	-
	tricresyl phosphate	-	-	-	-
Pigment	talc	-	-	8	2
	red iron oxide	-	-	2	2
	zinc oxide	-	-	5	-
	titanium dioxide	1	-	3	1
Antisagging agent	Disparlon A630-20X	4	3	3	2
	Bentone SD-2	-	-	-	1
Additive	trimethyl silanol	-	-	-	-
	KMP590	-	-	-	-
	Tinuvin 900	-	-	-	-
Solvent	xylene	2	10	5	15
	butyl acetate	-	-	-	-
Total		100	100	100	100

Table 8

		Example			
		9	10	11	12
Ingredient A	tall rosin	1	-	-	20
	gum rosin	-	-	20	15
	wood rosin	-	-	-	15
	Dimerex	-	20	-	20
	hydrogenated rosin	-	-	-	-
Ingredient B	polymer solution S <sub>1</sub>	-	30	-	-
	polymer solution S <sub>2</sub>	-	-	-	-
	polymer solution S <sub>3</sub>	-	-	-	-
	polymer solution S <sub>7</sub>	30	-	-	-
	polymer solution S <sub>8</sub>	-	-	-	-
	polymer solution S <sub>9</sub>	-	5	-	-
	polymer solution S <sub>10</sub>	-	-	25	-
	polymer solution S <sub>11</sub>	-	-	5	-
	polymer solution S <sub>12</sub>	-	-	-	2
Ingredient C	cuprous oxide	-	-	10	20
	copper thiocyanate	-	-	10	-
	Cu-Ni solid solution alloy	50	-	-	-
	2,4,5,6-tetrachloroisophthalonitrile	-	-	-	-
	N,N-dimethylchlorophenylurea	-	-	-	-
	4,5-dichloro-2-n-octylisothiazolin-3-one	-	-	-	-
	2-pyridinethiol-1-oxide zinc salt	-	-	15	-
	2-pyridinethiol-1-oxide copper salt	-	-	5	-
	2-(thiocyanomethylthio)benzothiazole	-	30	-	2
Plasticizer	chlorinated paraffin	1	-	-	-
	tricresyl phosphate	1	-	-	-
Pigment	talc	-	-	1	-
	red iron oxide	-	-	-	2
	zinc oxide	-	3	1	-
	titanium dioxide	-	1	-	-
Antisagging agent	Disparlon A630-20X	3	3	3	3
	Bentone SD-2	-	-	-	-
Additive	trimethyl silanol	-	-	-	-
	KMP590	-	-	-	-
	Tinuvin 900	-	-	-	-
Solvent	xylene	9	8	5	3
	butyl acetate	5	-	-	-
Total		100	100	100	100

Table 9

		Example			
		13	14	15	16
Ingredient A	tall rosin	-	-	-	20
	gum rosin	13	-	-	-
	wood rosin	-	-	5	-
	Dimerex	-	5	-	-
	hydrogenated rosin	-	5	-	-
Ingredient B	polymer solution S <sub>1</sub>	-	-	-	5
	polymer solution S <sub>2</sub>	4	-	-	-
	polymer solution S <sub>3</sub>	-	3	-	-
	polymer solution S <sub>11</sub>	-	-	20	-
	polymer solution S <sub>12</sub>	-	-	-	5
	polymer solution S <sub>13</sub>	4	-	15	-
	polymer solution S <sub>14</sub>	-	60	-	-
	polymer solution S <sub>15</sub>	-	-	20	-
	polymer solution S <sub>16</sub>	-	-	-	20
Ingredient C	cuprous oxide	68	-	20	-
	copper thiocyanate	-	-	-	20
	Cu-Ni solid solution alloy	-	-	-	-
	2,4,5,6-tetrachloroisophthalonitrile	-	-	-	-
	N,N-dimethylchlorophenylurea	-	-	-	-
	pyridine triphenylborane	-	3	-	-
	2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine	2	-	-	-
	2-pyridinethiol-1-oxide copper salt	-	-	1	-
	zinc dimethylthiocarbamate	-	2	-	-
Plasticizer	chlorinated paraffin	-	-	-	5
	tricresyl phosphate	-	-	2	-
Pigment	talc	-	-	-	2
	red iron oxide	-	-	-	-
	zinc oxide	-	1	1	5
	titanium dioxide	-	-	-	-
Antisagging agent	Disparlon A630-20X	2	3	3	3
	Bentone SD-2	1	-	-	-
Additive	trimethyl silanol	-	-	1	-
	KMP590	-	-	1	-
	Tinuvin 900	-	-	1	-
Solvent	xylene	6	18	10	15
	butyl acetate	-	-	-	-
Total		100	100	100	100



Table 10

		Example			
		17	18	19	20
Ingredient A	gum rosin	-	-	-	0.5
	wood rosin	-	-	2	-
	copper rosinate	3	-	-	-
	calcium rosinate	-	30	-	-
	zinc rosinate	-	30	-	-
Ingredient B	polymer solution S <sub>2</sub>	60	-	-	-
	polymer solution S <sub>4</sub>	-	-	-	40
	polymer solution S <sub>5</sub>	-	-	-	40
	polymer solution S <sub>6</sub>	-	-	-	-
	polymer solution S <sub>7</sub>	-	-	-	-
	polymer solution S <sub>8</sub>	-	27.4	-	3
	polymer solution S <sub>9</sub>	-	-	-	-
	polymer solution S <sub>10</sub>	-	-	-	-
	polymer solution S <sub>11</sub>	-	-	70	1
Ingredient C	cuprous oxide	5	-	15	5
	copper thiocyanate	3	-	-	-
	Cu-Ni solid solution alloy	-	-	2	-
	2,4,5,6-tetrachloroisophthalonitrile	-	0.2	-	1
	N,N-dimethylchlorophenylurea	-	-	-	-
	4,5-dichloro-2-n-octylisothiazolin-3-one	-	-	-	5
	N-(fluorodichloromethylthio)phthalimide	-	-	-	-
	pyridine triphenylborane	5	-	-	-
	2-pyridinethiol-1-oxide copper salt	5	-	2	1
Plasticizer	chlorinated paraffin	-	-	-	-
	tricresyl phosphate	-	-	-	-
Pigment	talc	2	-	-	-
	red iron oxide	3	1	1	2
	zinc oxide	1	-	-	-
	titanium dioxide	3	-	1	-
Antisagging agent	Disparlon A630-20X	2	1	2	3
	Bentone SD-2	1	-	-	-
Additive	trimethyl silanol	-	-	-	-
	KMP590	-	-	-	-
	Tinuvin 900	-	-	-	-
Solvent	xylene	7	0.4	5	2.5
	butyl acetate	-	10	-	-
Total		100	100	100	100

Table 11

		Comparative Example					
		1	2	3	4	5	6
Ingredient A	tall rosin	-	-	-	-	-	-
	gum rosin	20	20	20	-	5	20
	wood rosin	-	-	-	-	-	-
	Dimerex	-	-	-	-	-	-
	hydrogenated rosin	-	-	-	-	-	-
Blending polymer	Laroflex MP-15	10	-	-	-	-	-
	Pliolite S-5B	-	10	-	-	-	-
	Toyoparax A-70	-	-	10	-	-	-
	polymer solution S <sub>7</sub>	-	-	-	70	-	-
	polyisobutylene	-	-	-	-	5	-
	Polysol EVA-AD-3 (50% solution)	-	-	-	-	-	10
Ingredient C	cuprous oxide	30	30	30	20	37	37
	copper thiocyanate	-	-	-	-	-	-
	Cu-Ni solid solution alloy	-	-	-	-	-	-
	2,4,5,6-tetrachloroisophthalonitrile	-	-	-	-	-	-
	N,N-dimethylchlorophenylurea	-	-	-	-	-	-
	4,5-dichloro-2-n-octylisothiazolin-3-one	-	-	-	-	-	-
	N-(fluorodichloromethylthio) phthalimide	-	-	-	-	-	-
	pyridine triphenylborane	-	-	-	-	-	-
	2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine	-	-	-	-	-	-
	2-pyridinethiol-1-oxide zinc salt	-	-	-	-	-	-
	2-pyridinethiol-1-oxide copper salt	-	-	-	-	-	-
	2,4,6-trichlorophenylmaleimide	-	-	-	-	-	-
	3-iodo-2-propynylbutyl carbamate	-	-	-	3	-	-
	zinc dimethyldithiocarbamate	-	-	-	-	-	-
	2-(thiocyanomethylthio)benzothiazole	-	-	-	-	-	-
Plasticizer	chlorinated paraffin	-	-	-	-	-	-
	tricresyl phosphate	-	-	-	-	-	-
Pigment	talc	2	2	2	-	-	-
	red iron oxide	2	2	2	-	-	3
	zinc oxide	-	-	-	-	-	-
	titanium dioxide	1	1	1	-	-	-
Antisagging agent	Disparlon A630-20X	2	2	2	3	-	-
	Disparlon 4300	-	-	-	-	-	10
	Bentone SD-2	1	1	1	-	-	-
Additive	trimethyl silanol	-	-	-	-	-	-
	KMP590	-	-	-	-	-	-
	Tinuvin 900	-	-	-	-	-	-
Solvent	xylene	32	32	32	2	45	20
	solvent naphtha	-	-	-	-	5	-
	MLBK	-	-	-	-	3	-
	butyl acetate	-	-	-	-	-	-
Total		100	100	100	100	100	100

Each of the coating compositions prepared in Examples 1 to 20 and Comparative Examples 1 to 6 given above was subjected to a test for examining film surface residue layer formation, film erosion test, antifouling performance test, adhesion test, cracking resistance test, recoating test, and test for evaluating the ability to prevent marine-organism attachment over the out-fitting period, by the methods described below. The results obtained are shown in Tables 12 to 20 given later.

#### Test for Examining Film Surface Residue Layer Formation

Blasted steel panels (100 mm x 200 mm x 1 mm) were spray-coated twice with a tar-epoxy anticorrosive paint in a thickness of 125  $\mu$ m on a dry basis for each application, and further coated with a tar-vinyl sealer coat in a thickness of 70  $\mu$ m on a dry basis. The steel panels were then spray-coated twice with each coating composition in a thickness of 100  $\mu$ m for each application. The thus-coated steel panels were dried for 1 week in a thermo-hygrostatic chamber at 20°C and a humidity of 75%. Thus, six test pieces were produced for each coating composition.

The test pieces thus produced were immersed in artificial seawater. After immersion for each of 3, 6, 12, 18, and 24 months, the test pieces were pulled out of the water and cut. The cut surfaces were polished and then examined with a stereomicroscope to measure the thickness of any residue layer formed on each coating film surface.

Film Erosion Test

Steel panels (100 mm x 100 mm x 1 mm) which each had been coated on both sides with an anticorrosive paint were spray-coated, on the front side, with each coating composition twice in a thickness of 200  $\mu\text{m}$  on a dry basis for each application. The thus-coated steel panels were dried indoors at 20°C for 1 week to produce test pieces.

These test pieces were fixed to the outer circumferential surface of a cylindrical drum having a diameter of 50 cm. This drum was immersed in the seawater of Yura Bay, Sumoto, Hyogo, Japan at a depth of 1 m from the sea level, and rotated with a motor at such a rate that the peripheral speed of the drum was 16 knots. The reduction in coating film thickness caused by erosion was measured at an interval of 3 months over a period of 24 months. The average film erosion rate ( $\mu\text{m}/\text{month}$ ) for the initial 6 months and that for the period of from the 6th to the 24th month were calculated. An average film erosion rate of 3  $\mu\text{m}/\text{month}$  or higher correlates with satisfactory antifouling performance. In test pieces in which the average film erosion rate for the 6th to 24th month period was within the range of  $\pm 1$   $\mu\text{m}/\text{month}$  based on the average film erosion rate for the initial 6 months, the rate of film erosion was constant.

Antifouling Performance Test

Sandblasted steel panels (100 mm x 200 mm x 1 mm) coated beforehand with a tar-vinyl anticorrosive paint were spray-coated on both sides with each coating composition twice in a thickness of 240  $\mu\text{m}$  on a dry basis for each side. The coated panels were dried for 1 week in a thermo-hygrostatic chamber at 20°C and a humidity of 75% to produce test pieces. These test pieces were immersed in the seawater of Aioi Bay, Aioi, Hyogo, Japan, for 24 months to examine the change with time of the proportion of that area of the coating film which was covered with marine organisms attached thereto.

Adhesion Test

Blasted steel panels were spray-coated twice with a tar-epoxy anticorrosive paint in a thickness of 125  $\mu\text{m}$  on a dry basis for each application, and further coated with a tar-vinyl sealer coat in a thickness of 70  $\mu\text{m}$  on a dry basis. The coated steel panels were spray-coated twice with each coating composition in a thickness of 100  $\mu\text{m}$  on a dry basis for each application and then dried for 1 week in a thermo-hygrostatic chamber at 20°C and a humidity of 75% to produce test pieces.

These test pieces were immersed in artificial seawater. After immersion for each of 3, 6, 12, 18, and 24 months, the test pieces were pulled out of the water and subjected to a crosscut tape test in which the coating film was incised at an interval of 2 mm. Adhesion was evaluated as follows: the test pieces in which the number of peeled squares was 0 per 25 are indicated by ○ (acceptable), and those in which that number was 1 or larger per 25 are indicated by X (unacceptable).

Cracking Resistance Test

When the test pieces were pulled out of the artificial seawater in the adhesion test, each coating film was visually examined for cracks. The test pieces having no cracks are indicated by ○ (acceptable), while those having cracks are indicated by X (unacceptable).

Recoating Test

Steel panels (100 mm x 100 mm x 1 mm) which each had been coated on both sides with an anticorrosive paint were spray-coated, on the front side, with each coating composition twice in a thickness of 100  $\mu\text{m}$  on a dry basis for each application. The thus-coated steel panels were dried indoors at 20°C for 1 week. Thus, two test pieces were produced for each coating composition.

These test pieces were immersed in artificial seawater. After immersion for each of 12 and 24 months, the test pieces were pulled out of the water, washed with distilled water, and then dried indoors at 20°C for 1 week. Thereafter, each test piece was spray-coated twice with the same coating composition as that with which the test piece had been coated, in a thickness of 100  $\mu\text{m}$  on a dry basis for each application. The recoated test pieces were dried indoors at 20°C for 1 week. These test pieces were fixed to the outer circumferential surface of a cylindrical drum having a diameter of 50 cm. This drum was immersed in the seawater of Yura Bay, Sumoto, Hyogo, Japan, at a depth of 1 m from the sea level, and rotated with a motor at such a rate that the peripheral speed of the drum was 16 knots. After immersion for 1 week, the test pieces were pulled out of the seawater and examined for the peeling of the fresh coating film from the old one. The test pieces which suffered no peeling are indicated by ○ (acceptable), while those which suffered peeling are indicated by X (unacceptable).

Test for Evaluating the Ability to Prevent Marine-organism Attachment over Out-fitting Period

Sandblasted steel panels (100 mm x 300 mm x 1 mm) coated beforehand with a tar-vinyl anticorrosive paint were spray-coated on both sides with each coating composition twice in a thickness of 240  $\mu\text{m}$  on a dry basis for each side. The coated panels were dried for 1 week in a thermo-hygrostatic chamber at 20°C and a humidity of 75% to produce test pieces. These test pieces were immersed in the seawater of Owase Bay, Mie, Japan, over a period of 3 months from July to September, 1996 while being kept parallel to the water surface at a depth of 1 m from the sea level to examine the change with time of the proportion of that area of the coating film which was covered with marine organisms attached thereto.

Further, for the purpose of a comparison between Owase Bay and Aioi Bay in the degree of fouling by organisms during that period, and for the purpose of a comparison between vertical immersion and horizontal immersion, test pieces coated with the tar-vinyl anticorrosive paint only were immersed in both sea areas to compare the test pieces based on the weight of the organisms which adhered thereto.

Table 12

Test for examining film surface residue layer formation					
Thickness of residue layer on film surface ( $\mu\text{m}$ )					
	3 months	6 months	12 months	18 months	24 months
Example 1	0	0	0	0	0
Example 2	0	0	0	0	0
Example 3	0	0	0	0	0
Example 4	0	0	0	0	0
Example 5	0	0	0	0	0
Example 6	0	0	0	0	0
Example 7	0	0	0	0	0
Example 8	0	0	0	0	0
Example 9	0	0	0	0	0
Example 10	0	0	0	0	0
Example 11	0	0	0	0	0
Example 12	0	0	0	0	0
Example 13	0	0	0	0	0
Example 14	0	0	0	0	0
Example 15	0	0	0	0	0
Example 16	0	0	0	0	0
Example 17	0	0	0	0	0
Example 18	0	0	0	0	0
Example 19	0	0	0	0	0
Example 20	0	0	0	0	0
Comparative Example 1	5	5	10	10	10
Comparative Example 2	20	50	70	100	100
Comparative Example 3	5	10	30	70	100
Comparative Example 4	0	0	5	5	10
Comparative Example 5	15	50	90	120	140
Comparative Example 6	10	30	70	90	100

Table 13

		Film erosion test							
		Film thickness reduction ( $\mu\text{m}$ )							
		3 months	6 months	9 months	12 months	15 months	18 months	21 months	24 months
Example	1	15	31	44	61	77	88	103	125
	2	28	60	88	115	151	181	212	243
	3	12	25	36	49	58	74	86	99
	4	8	18	29	38	48	57	65	76
	5	36	72	108	144	180	216	252	288
	6	20	41	66	82	102	128	149	171
	7	26	50	70	95	119	148	172	195
	8	30	65	102	130	168	201	233	267
	9	18	37	56	74	95	112	129	144
	10	39	76	117	150	191	230	269	309
	11	13	29	46	62	71	91	105	121
	12	26	55	81	106	136	165	191	219
	13	27	53	83	102	133	161	189	216
	14	44	89	133	179	222	273	316	362
	15	23	48	71	99	118	142	169	195
	16	46	95	142	193	240	289	338	386
	17	31	59	90	118	152	179	212	235
	18	11	23	38	50	58	70	85	101
	19	35	70	103	142	182	214	250	285
	20	24	47	72	98	121	140	170	189
Comparative Example	1	8	15	17	18	20	22	23	23
	2	0	0	1	2	2	2	2	2
	3	20	59	77	82	85	87	90	91
	4	7	19	27	37	44	52	52	52
	5	0	1	2	4	5	5	5	5
	6	29	59	78	92	95	100	102	103

Table 14

	Film erosion test	
	Average film erosion rate ( $\mu\text{m}/\text{month}$ )	
	initial 6 months	from 6th to 24th month
Example 1	5.3	5.1
Example 2	10.7	10.3
Example 3	4.3	4.1
Example 4	3.3	3.2
Example 5	12.0	12.0
Example 6	7.0	7.2
Example 7	8.0	8.2
Example 8	11.7	11.2
Example 9	6.3	6.0
Example 10	12.3	12.9
Example 11	5.3	5.0
Example 12	9.7	9.2
Example 13	8.7	9.0
Example 14	15.0	15.2
Example 15	8.3	8.1
Example 16	16.3	16.2
Example 17	9.3	9.9
Example 18	4.0	4.1
Example 19	11.7	12.0
Example 20	7.7	7.9
Comparative Example 1	2.3	0.5
Comparative Example 2	0.0	0.1
Comparative Example 3	13.0	1.5
Comparative Example 4	4.0	2.0
Comparative Example 5	0.3	0.2
Comparative Example 6	10.0	2.2

Table 15

		Antifouling performance test				
		Proportion of area covered with marine organisms (%)				
		3 months	6 months	12 months	18 months	24 months
5	Example 1	0	0	0	0	0
10	Example 2	0	0	0	0	0
	Example 3	0	0	0	0	0
	Example 4	0	0	0	0	0
	Example 5	0	0	0	0	0
15	Example 6	0	0	0	0	0
	Example 7	0	0	0	0	0
	Example 8	0	0	0	0	0
20	Example 9	0	0	0	0	0
	Example 10	0	0	0	0	0
	Example 11	0	0	0	0	0
25	Example 12	0	0	0	0	0
	Example 13	0	0	0	0	0
	Example 14	0	0	0	0	0
	Example 15	0	0	0	0	0
30	Example 16	0	0	0	0	0
	Example 17	0	0	0	0	0
	Example 18	0	0	0	0	0
35	Example 19	0	0	0	0	0
	Example 20	0	0	0	0	0
	Comparative Example 1	10	20	100	100	100
	Comparative Example 2	5	30	60	100	100
40	Comparative Example 3	0	20	50	90	100
	Comparative Example 4	0	0	0	0	30
	Comparative Example 5	10	30	100	100	100
45	Comparative Example 6	0	0	30	100	100

Table 16

	Adhesion test				
	3 months	6 months	12 months	18 months	24 months
Example 1	○	○	○	○	○
Example 2	○	○	○	○	○
Example 3	○	○	○	○	○
Example 4	○	○	○	○	○
Example 5	○	○	○	○	○
Example 6	○	○	○	○	○
Example 7	○	○	○	○	○
Example 8	○	○	○	○	○
Example 9	○	○	○	○	○
Example 10	○	○	○	○	○
Example 11	○	○	○	○	○
Example 12	○	○	○	○	○
Example 13	○	○	○	○	○
Example 14	○	○	○	○	○
Example 15	○	○	○	○	○
Example 16	○	○	○	○	○
Example 17	○	○	○	○	○
Example 18	○	○	○	○	○
Example 19	○	○	○	○	○
Example 20	○	○	○	○	○
Comparative Example 1	X	X	X	X	X
Comparative Example 2	X	X	X	X	X
Comparative Example 3	X	X	X	X	X
Comparative Example 4	○	○	○	○	X
Comparative Example 5	X	X	X	X	X
Comparative Example 6	X	X	X	X	X



Table 17

		Cracking resistance test				
		3 months	6 months	12 months	18 months	24 months
Example 1		○	○	○	○	○
Example 2		○	○	○	○	○
Example 3		○	○	○	○	○
Example 4		○	○	○	○	○
Example 5		○	○	○	○	○
Example 6		○	○	○	○	○
Example 7		○	○	○	○	○
Example 8		○	○	○	○	○
Example 9		○	○	○	○	○
Example 10		○	○	○	○	○
Example 11		○	○	○	○	○
Example 12		○	○	○	○	○
Example 13		○	○	○	○	○
Example 14		○	○	○	○	○
Example 15		○	○	○	○	○
Example 16		○	○	○	○	○
Example 17		○	○	○	○	○
Example 18		○	○	○	○	○
Example 19		○	○	○	○	○
Example 20		○	○	○	○	○
Comparative Example 1		X	X	X	X	X
Comparative Example 2		X	X	X	X	X
Comparative Example 3		X	X	X	X	X
Comparative Example 4		○	○	○	○	X
Comparative Example 5		X	X	X	X	X
Comparative Example 6		X	X	X	X	X

Table 18

	Recoating test	
	old-film immersion period, 12 months	old-film immersion period, 24 months
Example 1	○	○
Example 2	○	○
Example 3	○	○
Example 4	○	○
Example 5	○	○
Example 6	○	○
Example 7	○	○
Example 8	○	○
Example 9	○	○
Example 10	○	○
Example 11	○	○
Example 12	○	○
Example 13	○	○
Example 14	○	○
Example 15	○	○
Example 16	○	○
Example 17	○	○
Example 18	○	○
Example 19	○	○
Example 20	○	○
Comparative Example 1	X	X
Comparative Example 2	X	X
Comparative Example 3	X	X
Comparative Example 4	X	X
Comparative Example 5	X	X
Comparative Example 6	X	X

Table 19

Test for evaluating the ability to prevent marine-organism attachment over out-fitting period			
Proportion of area covered with marine organisms (%)			
	1 month	2 months	3 months
Example 1	0	0	0
Example 2	0	0	0
Example 3	0	0	0
Example 4	0	0	0
Example 5	0	0	0
Example 6	0	0	0
Example 7	0	0	0
Example 8	0	0	0
Example 9	0	0	0
Example 10	0	0	0
Example 11	0	0	0
Example 12	0	0	0
Example 13	0	0	0
Example 14	0	0	0
Example 15	0	0	0
Example 16	0	0	0
Example 17	0	0	0
Example 18	0	0	0
Example 19	0	0	0
Example 20	0	0	0
Comparative Example 1	50	100	100
Comparative Example 2	40	60	100
Comparative Example 3	100	100	100
Comparative Example 4	10	40	100
Comparative Example 5	80	100	100
Comparative Example 6	30	80	100

Table 20

Comparison in the degree of fouling by organisms with test pieces uncoated with antifouling paint for preventing marine-organism attachment			
	Weight of adherent marine organisms (kg)		
	1 month	2 months	3 months
Owase (horizontal immersion)	1.5	2.2	3.2
Owase (vertical immersion)	0.4	1.0	1.8
Aioi (horizontal immersion)	0.3	0.7	1.2
Aioi (vertical immersion)	0.2	0.5	1.0
The proportion of the area covered with marine organisms was 100% in each case. * Owase: Owase Bay, Mie, Japan Aioi : Aioi Bay, Hyogo, Japan			

As apparent from the results given in Tables 12 to 20, all the comparative compositions containing prior art rosin-blending polymers, namely the composition of Comparative Example 1 which contained "Laroflex MP-15" (trade name of BASF AG; vinyl chloride resin), the composition of Comparative Example 2 (corresponding to an Example of JP-A-60-28456) which contained "Pliolite S-5B" (trade name of The Goodyear Tire & Rubber Company; styrene-butadiene rubber), the composition of Comparative Example 3 (corresponding to another Example of JP-A-60-28456) which contained "Toyoparax A-70" (trade name of Tosoh Corp.; chlorinated paraffin resin), the composition of Comparative Example 5 (corresponding to an Example of JP-A-50-135125) which contained polyisobutylene, and the composition of Comparative Example 6 (corresponding to still another Example of JP-A-60-28456) which contained "Polysol EVA-AD-3" (trade name of Showa Highpolymer Co., Ltd.; ethylene/vinyl acetate copolymer, 50% solution), and the coating composition of Comparative Example 4 (corresponding to an Example of U.S. Patent 5,436,284) not containing ingredient A of the present invention gave coating films on which a residue layer was formed in long-term immersion and which were unsatisfactory in both film erosion rate and antifouling performance, although the coating films obtained from some of these comparative compositions showed satisfactory erodibility for several months from the initiation of immersion. The comparative coating compositions were also defective in cracking resistance, adhesion, suitability for recoating, etc.

The results further show that in contrast to those comparative compositions, the coating compositions of Examples 1 to 20, which contained any of various rosin compounds in combination with any of solutions S<sub>1</sub> to S<sub>12</sub> of hydrolyzable polymers containing organosilyl ester groups, gave coating films which were free from the formation of a residue layer thereon over long-term immersion and were satisfactory in all of film erosion rate, antifouling performance, cracking resistance, adhesion, suitability for recoating, and the ability to prevent marine-organism attachment over the out-fitting period. Namely, the results show that the coating compositions according to the present invention combined excellent performances.

As demonstrated above, the coating composition of the present invention is applicable to underwater structures required to be protected from fouling and damage by marine organisms, such as ship bottoms, fishing nets, and cooling water pipes, and is further usable for the sludge diffusion prevention in ocean civil engineering works and for other purposes. The coating film obtained from the composition does not form a residue layer thereon over long-term immersion, and is hence free from physical defects such as cracks and peeling and capable of maintaining a sufficiently high rate of film erosion and preventing the attachment of marine organisms over long. In particular, the coating film has the satisfactory ability to prevent marine-organism attachment over the out-fitting period. The coating film further has satisfactory suitability for recoating.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

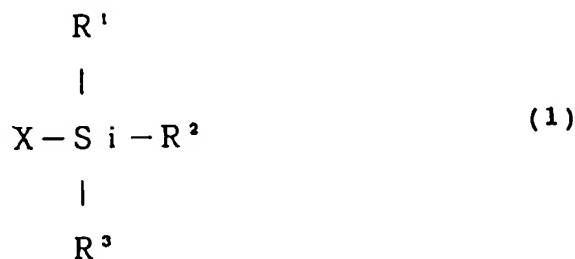
## Claims

1. A coating composition comprising, as essential components,

(A) at least one rosin compound selected from rosins, rosin derivatives and rosin metal salts;

(B) at least one polymer containing an organosilyl ester group,  
wherein said at least one polymer is composed of:

- i) a polymer obtained from at least one of monomers A represented by formula (1);
- ii) a polymer obtained from at least one of said monomers A and at least one of polymerizable monomers other than said monomers A; or
- iii) a mixture of the polymers i) and ii),



wherein  $R^1$ ,  $R^2$  and  $R^3$  are the same or different and each represents an alkyl group or an aryl group; and X represents an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group, a fumaroyloxy group, an itaconoyloxy group or a citraconoyloxy group; and

(C) an antifoulant.

2. A coating composition according to claim 1, wherein the proportion of said at least one rosin compound to said at least one polymer containing an organosilyl ester group is from 1/99 to 99/1, by weight on a solid basis.
3. A coating composition according to claim 1, wherein said at least one polymer containing an organosilyl ester has a weight-average molecular weight of from 1,000 to 150,000.
4. A coating composition according to claim 1, wherein said antifoulant is used in an amount of from 0.1 to 80% by weight based on the total amount of all solid ingredients in the coating composition.
5. A coating composition according to claim 1, wherein said at least one polymer (B) contains said monomers A in an amount of 1 to 100% by weight and said at least one of polymerizable monomers other than said monomers A in an amount of 99 to 0% by weight.